

**Workshop: “Environmental Redox:  
Fundamental Aspects of Electron and  
Atom Transfer in Solution”  
PNNL, 21-22 Sept 1998**

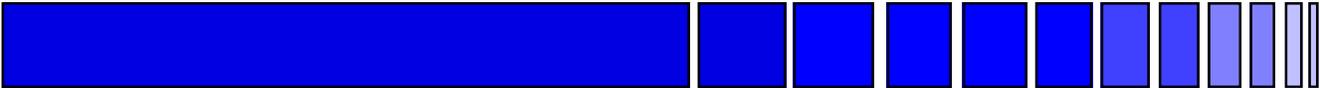


**Chemistry and Metal Ions  
in Water: Calculations and  
'Quasi-Chemical Theories'  
of Solution Chemistry**

**R. L. Martin, P. J. Hay, and L. R. Pratt**

**see:** R. L. Martin, P. J. Hay, and L. R. Pratt, *J. Phys. Chem. A* **102**, 3565-3573 (1998): “Hydrolysis of ferric ion in water and conformational equilibrium.”

# Outline



## ● Theory:

- **Electronic structure: metal ions + inner solvation shell**
- **Hydration: inner solvation shell + dielectric**  
→ “quasi-chemical” theories.

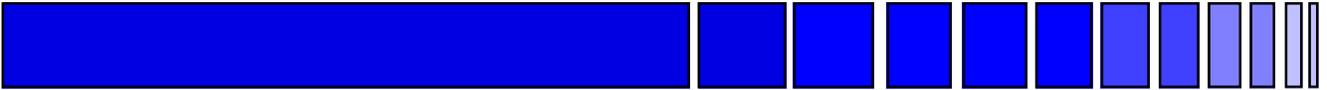
## ● Some examples:

- **Hydration and hydrolysis of hexa-aquoferrous ion**
- **Water self-ionization (used everywhere)**
- **Standard electrode potentials, ferrous-ferric, and actinyl ions**

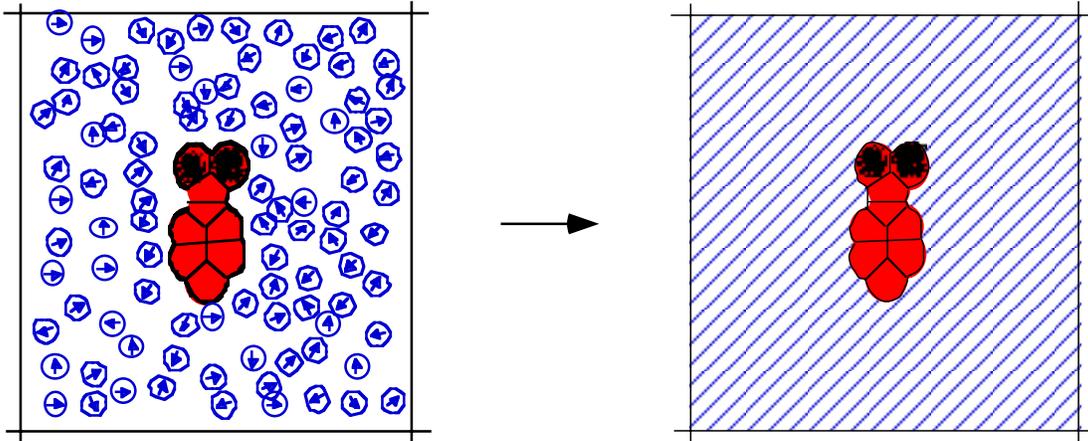
## ● Hydration theory and electronic structure calculations

- **Status of dielectric approaches**
- **Quasi-chemical approximation**

# Dielectric Model

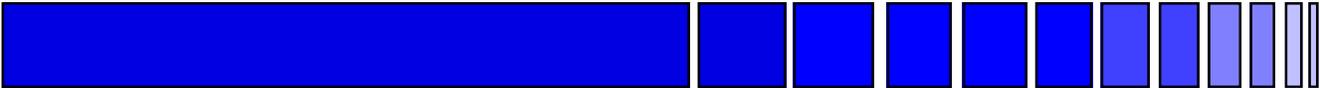


- hydration model that couples simply to electronic structure calculatons



$$\nabla \cdot \boldsymbol{\varepsilon}(\mathbf{r}) \nabla \Phi(\mathbf{r}) = -4\pi \rho(\mathbf{r})$$

# An example



## ● Absolute hydration free energy of the $\text{Fe}^{3+} (aq)$ ion

- experiment:  $\{-1019, -1039\}$  kcal/mol
- calculation:  $-1020$  kcal/mol



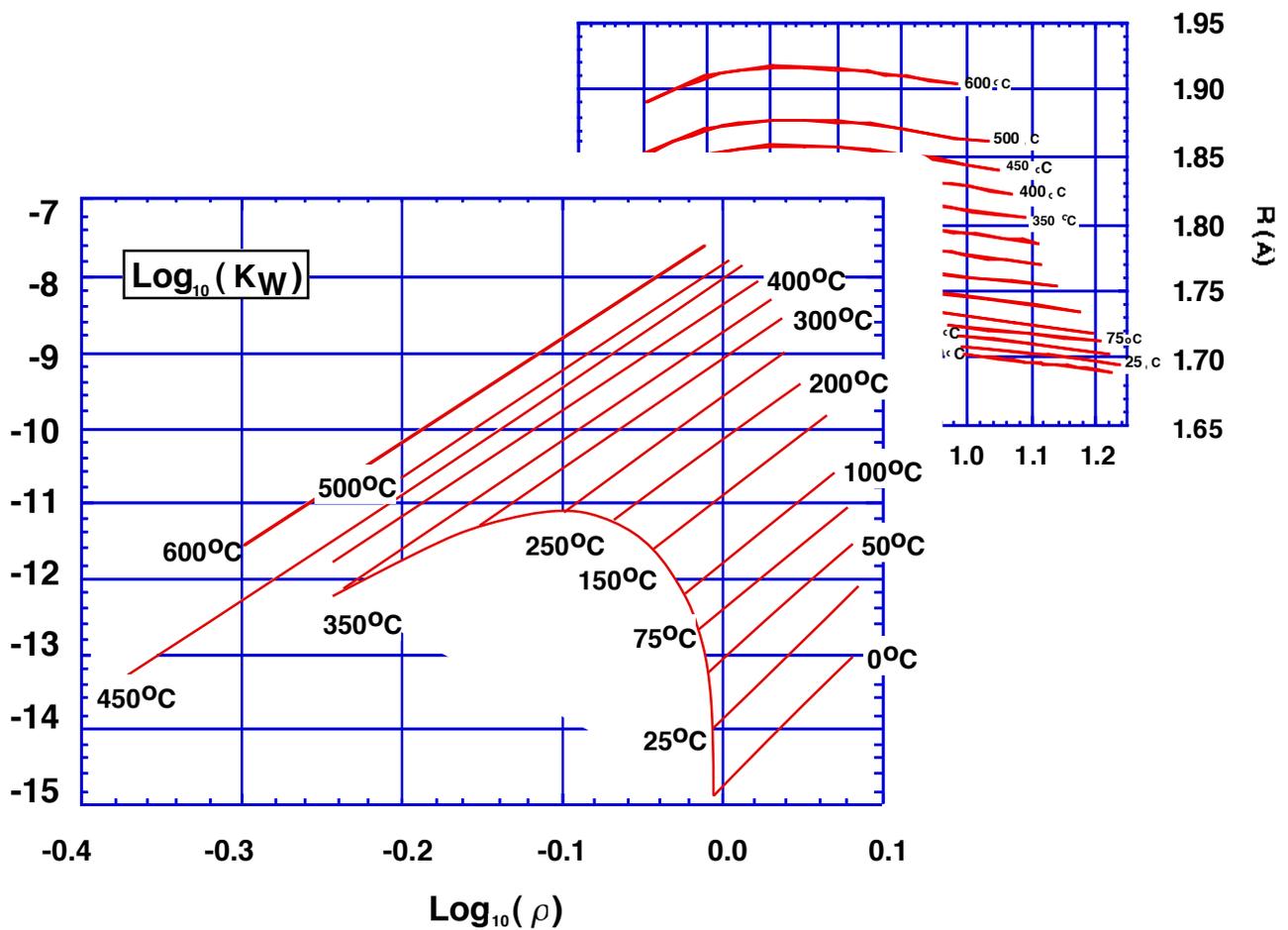
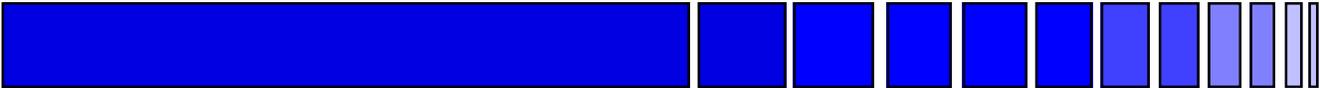
⊗  $6 \mu_{\text{ligand}} ("p=1354 \text{ atm}") \Delta \mu_{\text{complex}}$

$$\begin{aligned} \Delta \mu_{\text{Fe}^{3+}} &= -RT \ln K_6 + \Delta \mu_{\text{complex}} - 6 \mu_{\text{ligand}} \\ &= -RT \ln \left[ K_6 \left( \frac{\rho_{\text{ligand}} RT}{1 \text{ atm}} \right)^6 \right] \\ &\quad + \Delta \mu_{\text{complex}} - 6 \Delta \mu_{\text{ligand}} \end{aligned}$$

-629 kcal/mol

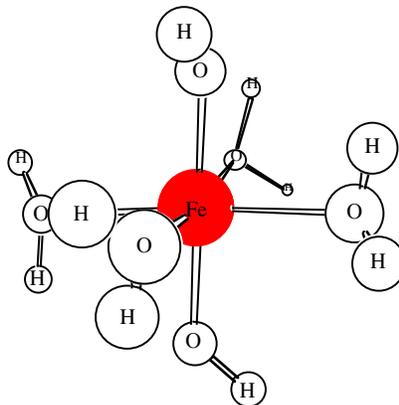
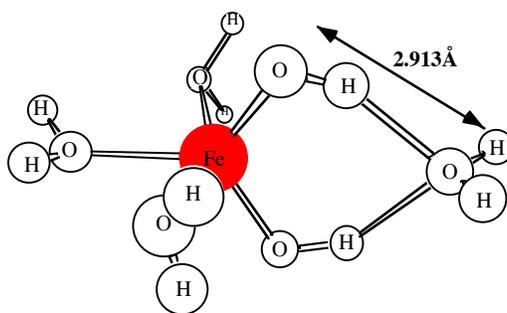
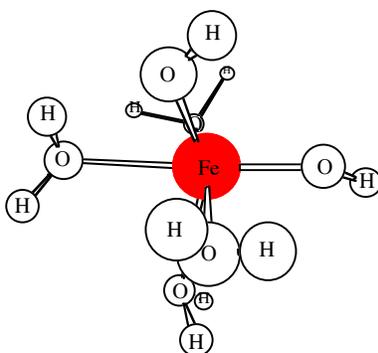
-391 kcal/mol  
-1020 kcal/mol

# calibration: $pK_w$





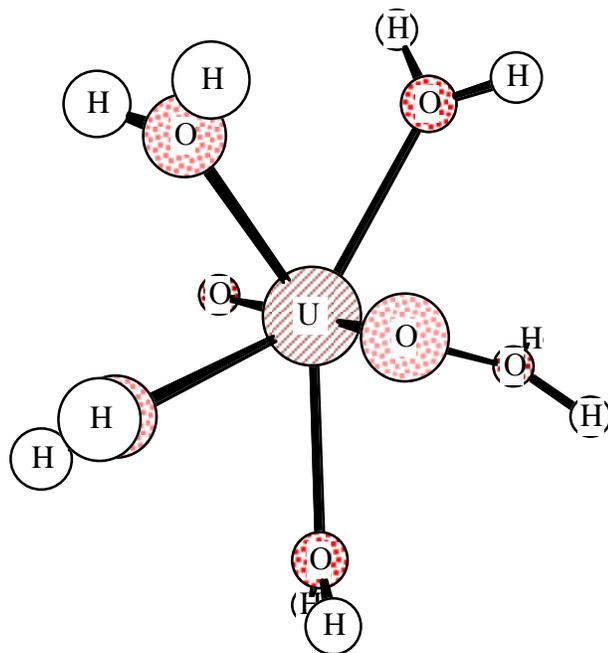
# isomeric structures for $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$



# Uranyl hydrolysis



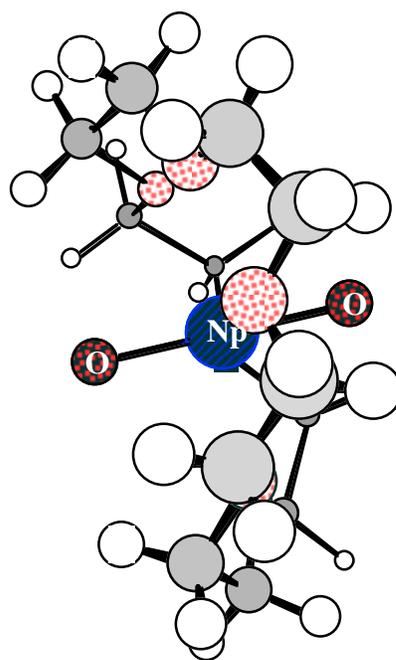
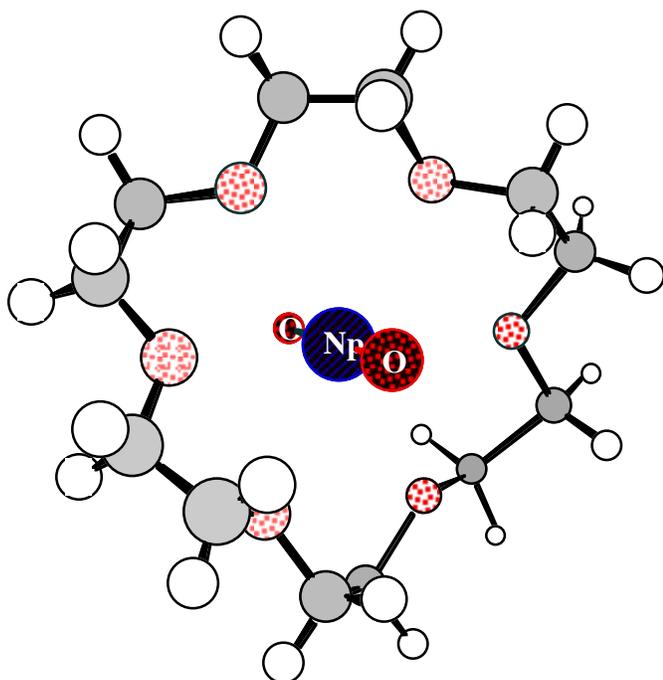
- actinide ECP's have been generated: P. J. Hay, R. L. Martin, *J. Chem. Phys.* 109, 3875 (1998)
- similar (rough) agreement with experiment, i.e., within about 15 kcal/mol.
- experimentalists are willing to entertain some argument whether the hydration number (5 above) is perfectly known.
- uncertainties begin to pile-up here on the theoretical side too.



# Hydration structures and actinides



- Other actinide structures have been studied,<sup>†</sup> e.g.,  $\text{NpO}_2^+$  ... 18-crown-6

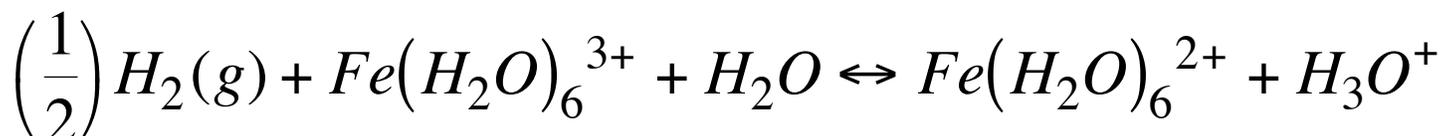


<sup>†</sup> other actinide complexes: G. Schreckenbach, R. L. Martin, P. J. Hay, *Inorg. Chem.* 37, 4442 (1998).

# Standard electrode potentials



- Set-up consistent with formulation for proton transfer, i.e., for ferric-ferrous:

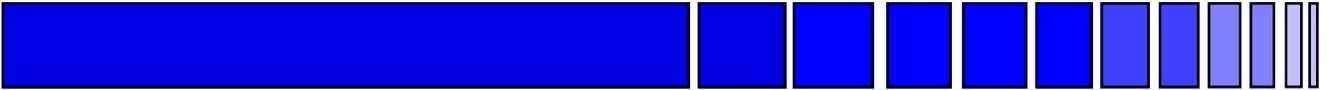


- $E^{(0)} = - \Delta G^{(0)}/nF$
- $Fe^{3+} - Fe^{2+}$ : 0.76 V (vs. 0.77 V, experiment†)

† Chemical Analysis, Laitinen, p. 280

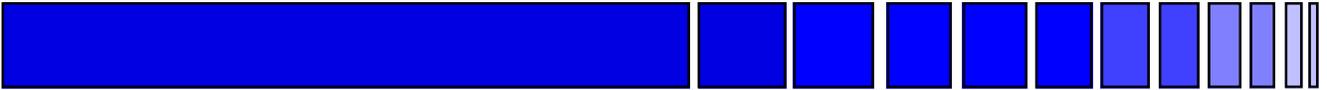


# Summary

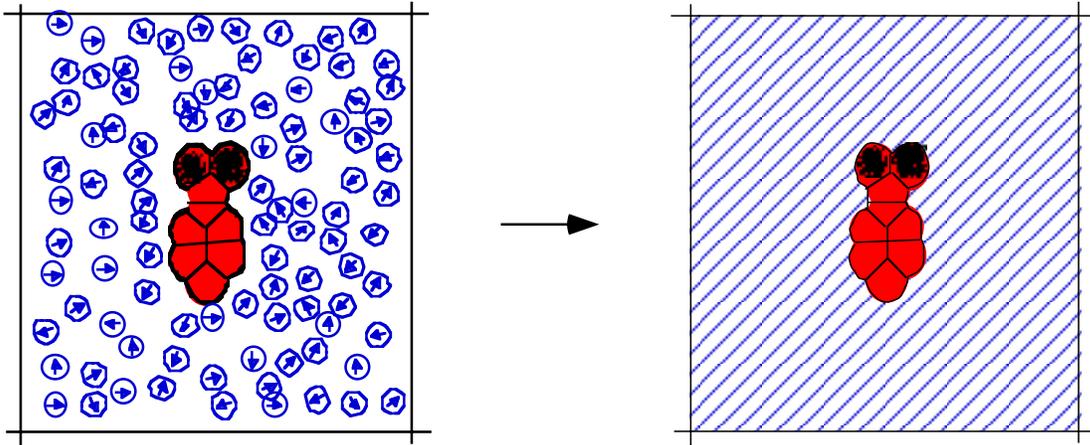


- **Starting with the hexa-aquo ferric test case, the calculations seem clear, agreement with experiment is satisfactory.**
- **As we move away from that well-known case, the agreement with experimental thermochemistry appears to deteriorate. Several reasons for this deterioration are available, assessment of the various possibilities is preliminary only.**
- **Maybe we need a definition of a next test case for theoretical and experimental study.**
- **Next topic here is hydration theory ...**

# Dielectric Model

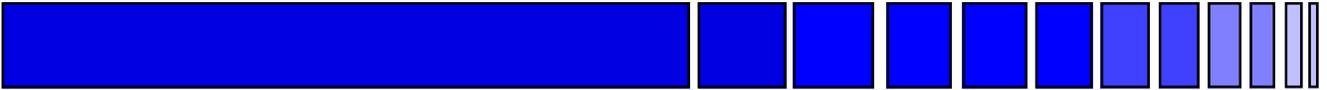


- “Everything should be made as simple as possible, but no simpler.”  
A. Einstein



$$\nabla \cdot \boldsymbol{\varepsilon}(\mathbf{r}) \nabla \Phi(\mathbf{r}) = -4\pi \rho(\mathbf{r})$$

# Dielectric Model



## ● pro:

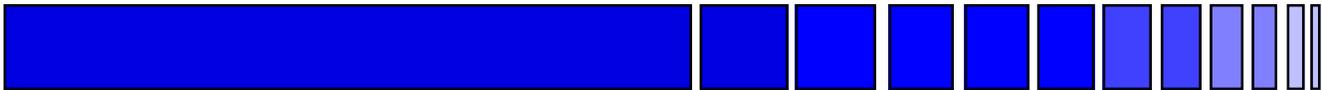
- **physical - can be derived from a Hamiltonian. (in more than one way!)**
- **practical - reasonably treats huge effects that can't be ignored**
- **chemical - can simultaneously include reasonable chemistry**
- **empirical - parameterizations (radii) are not unreasonable**

## ● con:

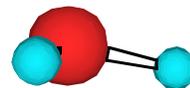
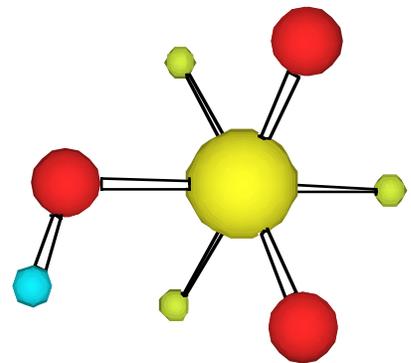
- **careful, molecular scale validation is MIXED**
- **often 100% empirical - parameters (radii) must be reconsidered for EVERY new result; results are sensitive to parameters and any physical result (correct or not) can be reproduced**



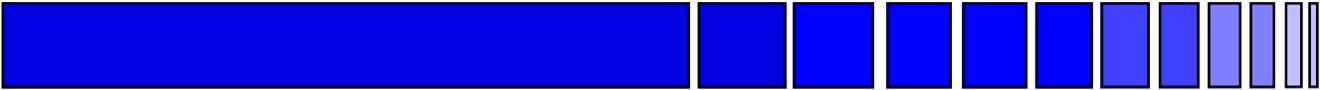
# Physical conclusions from simulations



- Dielectric models of hydration fail on a molecular scale when proton (H) structures near the solute lead to non-gaussian fluctuations of electrostatic potentials
- easiest examples to get “right” are classic cations, *e.g.* Na<sup>+</sup>
  - neutral, polar, H-bonding molecules, *e.g.* H<sub>2</sub>O or imidazole are more difficult cases for dielectric models when tested on a molecular scale. However, hydration free energies are smaller than for ions.
  - negative ions are again a problem and the hydration free energies will be large. But here chemistry will be more important also for negative ions of first importance, *e.g.* HCO<sub>3</sub><sup>-</sup>.



# How to test?



- **Dielectric models are simplified ...**

- second order perturbation theory,
- or (equivalently) linear response,
- or (equivalently) gaussian fluctuation of electrostatic potentials.

- **For a spherical ion**

- Born model

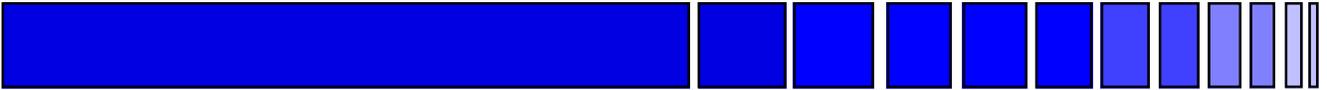
$$\Delta\mu = -\frac{q^2}{2R} \left( \frac{\varepsilon - 1}{\varepsilon} \right)$$

- second order perturbation theory

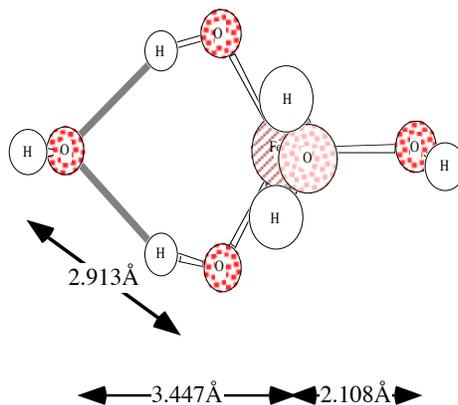
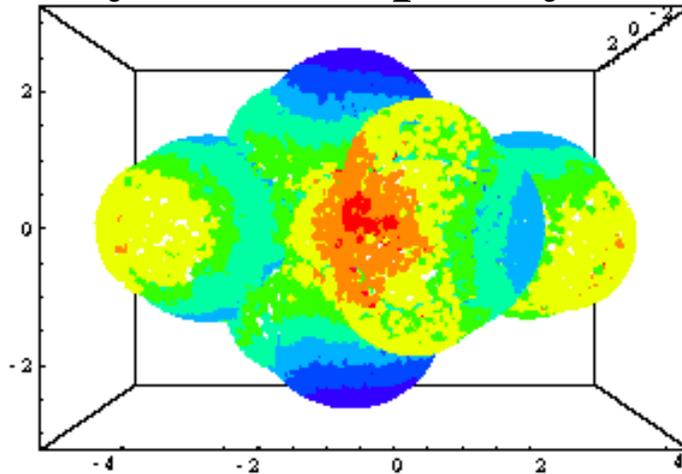
$$\Delta\mu = \Delta\mu_0 + q\langle\Phi\rangle_0 - \frac{\beta q^2}{2} \langle\delta\Phi^2\rangle_0$$

- **Test those approaches and avoid the issue of empirical adjustment of radii.**

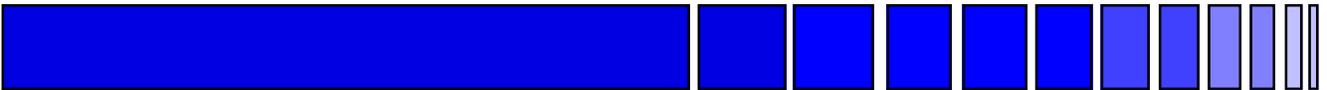
# Quasi-chemical



- yet need a way to start with liquid theory, include chemistry, and calculate
- Chemistry - it'll surprise you.

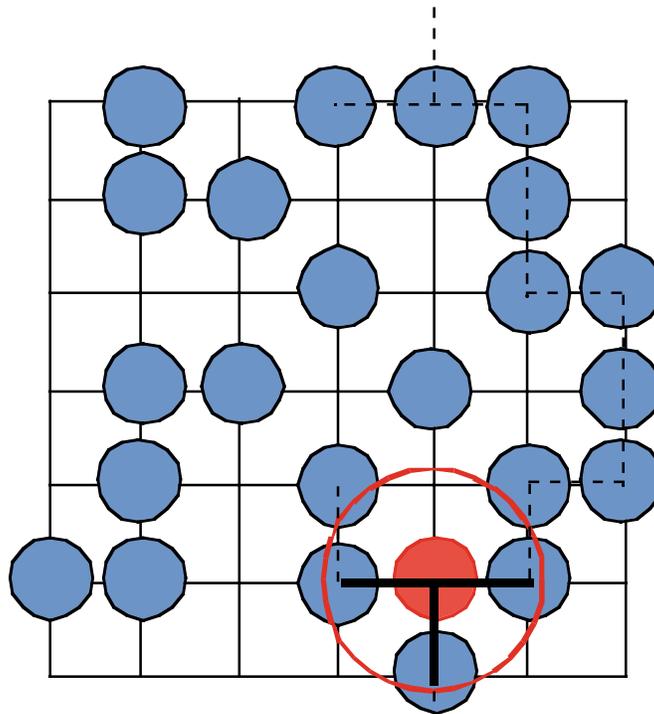


# clustering...



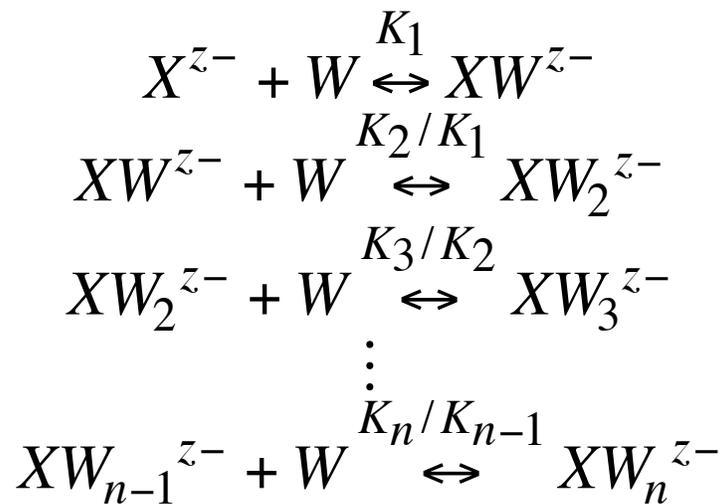
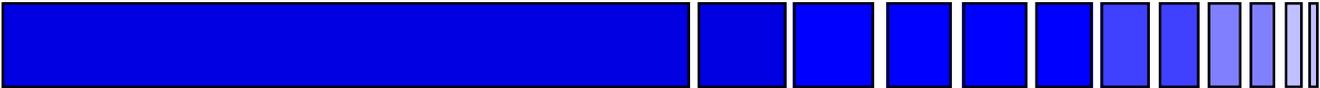
## ● local (not spanning) clusters

- “Quasi-chemical theories of associated liquids,” Pratt & LaViolette, *Molec. Phys.* 94, 909 (1998)



- “One of the principal objects of theoretical research in my department of knowledge is to find the point of view from which the subject appears in its greatest simplicity.” J. W. Gibbs

# Quasi-chemical formulation

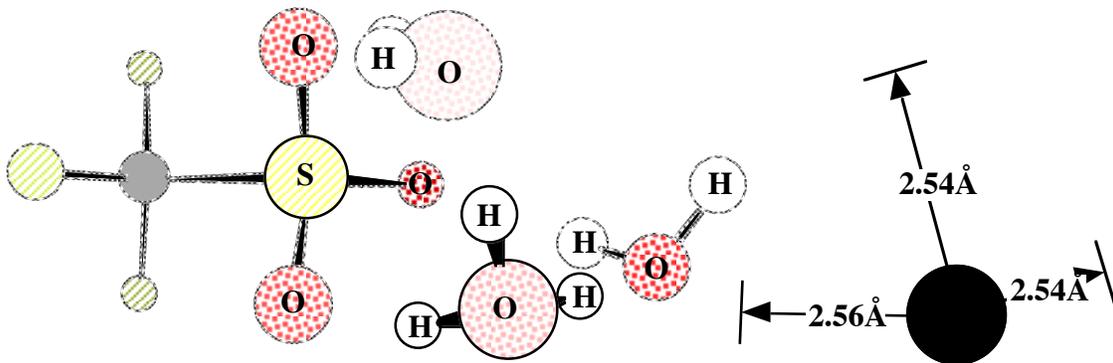
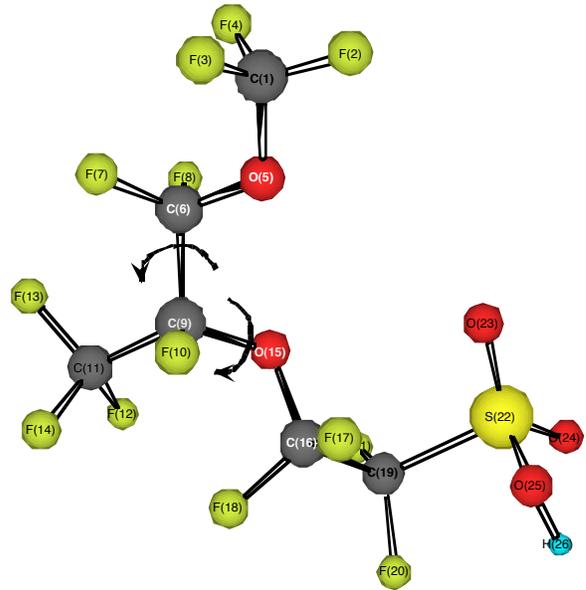
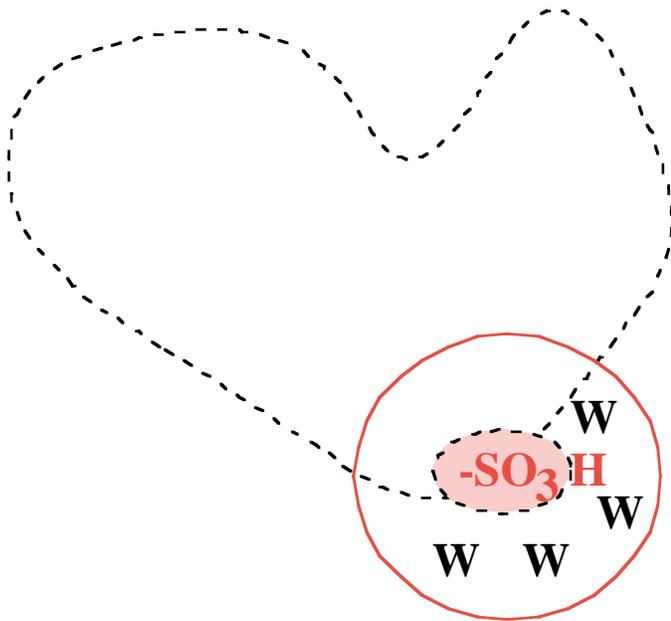
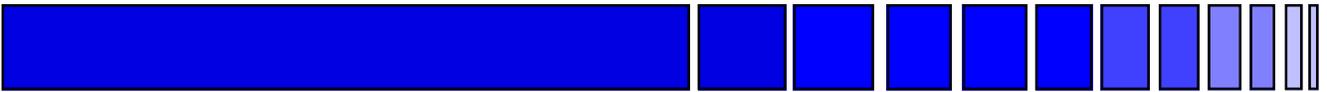


$$\begin{aligned}
 \mu_{X^{z-}} &= RT \ln \left[ \frac{\rho_{X^{z-}}}{(q_{X^{z-}} / V)} \right] \\
 &\quad - RT \ln p_0 \\
 &\quad - RT \ln \left[ \sum_{n=0} K_n \rho_W^n \right]
 \end{aligned}$$

ideal,  
  
packing,  
chemistry,  
electrostatics,  
entropy.

- $p_0$  = probability of an open cavity for the cluster volume, e.g.  $(1 - \rho v)$ , entropy too.

# extended molecules?



# Conclusions: hydration theory and chemistry



- **Dielectric models for hydration breakdown first because of near neighbor protons that lead to non-gaussian fluctuations of electrostatic potentials.**
- **Explicit consideration of near neighbor water molecules as in multi-gaussian models<sup>†</sup> repairs (not for negative ions) this primary failure of dielectric models.**
  - <sup>†</sup> G. Hummer, L. R. Pratt, and A. E. Garcia, *J. Am. Chem. Soc.* 118, 8523 (1997): “Multistate gaussian model for polar and ionic hydration .”
- **Quasi-chemical approaches again treat near neighbor water molecules specially but permit straightforward application of electronic structure calculations on inner solvation shells. This should also fix problems with negative ions.**